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(54) [Title of the Invention]

Polyester Resin Composition for Calendering and Sheet Prepared from It

(57) [Abstract]

[Object]

The object is to provide a polyester resin composition enabling excellent calendering sheet preparation with extremely good characteristics of not only excellent peelability of sheets from rollers but also excellent takeup ability of molten sheets from calender rollers to cooling rollers and at the same time, providing excellent transparency of sheets prepared.

[Means to Accomplish the Object]

The polyester composition is characterized by comprising 100 parts by weight of amorphous polyester, 0.01-5 parts by weight of lubricant and 0.01-50 parts by weight of an agent for increasing molecular weight and the weight-average molecular weight of the polymer component of the calendered sheets being increased by 5% or more from that of the polyester before calendering.

[Patent Claims]

[Claim 1]

A polyester composition for calendering characterized by comprising 100 parts by weight of amorphous polyester, 0.01-5 parts by weight of lubricant and 0.01-50 parts by weight of an agent for increasing molecular weight and the weight-average molecular weight of the polymer component of the calendered sheets being increased by 5% or more from that of the polyester before calendering.

[Claim 2]

A sheet characterized by being prepared by processing the resin composition of Claim 1.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

This invention pertains to a polyester composition and its sheet having excellent characteristics in the case of polyester calendering such as roller peelability, long-run workability and thermal stability, especially takeup ability and being suitable for calendering useful for various sheets and films such as shrinkable films for foods, cosmetics, beverages, etc., flavor-retaining heat-sealable films, oil-resistance multilayer films, etc., especially sheets and films of industrial applications.

[0002]

[Prior Art]

Previously, vinyl chloride-type sheets (including films) have been used in various fields of applications because of low cost and excellent transparency. As a method for processing these sheets, the extrusion molding and calender molding have been known. In the extrusion molding compared with the calender molding, the workability (moldability) of the resin is affected by die lip friction, the precision is poor with respect to thickness, width, flow direction, etc., and at the same time, the method is not suitable for manufacturing. Consequently, the latter method is frequently used because of the above reasons with respect to productivity and product quality. The softness of vinyl chloride-type sheets or films can be freely adjustable by adding a plasticizer. One typical example of the applications includes decorative sheets (including films, same below) with a wood vein figure printed to improve design of wood materials. However in recent years, there is a tendency of vinyl chloride-type sheets (including films, same below) being replaced by other materials because of various reasons. Among various replacement materials, polyester is one of the most prevailing materials with respect to physical properties, costs, etc. However, there is the following significant problem to be solved before using polyester as a replacement.

[0003]

Specifically, the calender molding, which have been widely used as a molding method for vinyl chloride-type sheets, is difficult to be applied for molding polyester sheets or films. Previ-

ously, polyester resins have been molded to sheets or films by using mostly extrusion molding because of the ease of processing. In the case of calendering of polyester resins, the molding process is difficult because of the adhesion of thermally plasticized resins to rollers is relatively strong becoming liable to cause the resins to adhere on rollers. Therefore, it has been attempted to reduce this adhesion to rollers by adding various kinds of lubricants. Specific examples of such a lubricant include hydrocarbon lubricants such as polyethylene wax, paraffin wax, etc., higher fatty acid-type lubricants, higher alcohol-type lubricants, metal soaps of higher fatty acids, fatty acid amide-type lubricants, ester lubricants and others. For example, in Japanese Kokai Patent Application Publication Nos. Hei 11[1999]-343,353, 2000-136,294, 2000-186,191, 2000-302,951, 2001-64,496 and 2001-4,019 and US-6,068,910, various lubricants were used for amorphous polyethylene terephthalate prepared by copolymerization with cyclohexanedimethanol to prepare sheets by carrying out calendering. The peelability from rollers was described to be good in some cases, but for the practical applications, there remained a significant problem requiring a solution. Specifically, the inventors of this invention carried out a calendering test by using the amorphous polyester and lubricants disclosed, and the peeling from the calendering rollers was found achievable if the amount of lubricant added was increased, but when the molten sheet was peeled off from the calendering rollers, taken up and sent to cooling rollers, the strength of the resin structure was found insufficient causing so-called "sagging" due to the own weight of the sheet and consequently, a problem of not being able to carry out the takeup from the calendering rollers to cooling rollers smoothly. Namely, the problem is the takeup ability of the molten sheet being insufficient.

[0004]

[Object of the Invention]

Considering the circumstances described above, the object of this invention is to provide a polyester resin composition enabling excellent calendering sheet preparation with extremely good characteristics of not only excellent peelability of sheets from rollers but also excellent takeup ability of molten sheets from calender rollers to cooling rollers and at the same time, providing excellent transparency of sheets prepared.

[0005]

[Means to Accomplish the Object]

The inventors of this invention studied diligently to accomplish the above object; as a result, they found that it was possible, at the time of calendering, to obtain not only a good peelability from calendering rollers but also excellent takeup ability from calender rollers and good transparency of the sheet prepared; and they arrived at this invention.

[0006]

Specifically, this invention has the following characteristics.

(1) A polyester composition for calendering characterized by comprising 100 parts by weight of amorphous polyester, 0.01-5 parts by weight of lubricant and 0.01-50 parts by weight of an agent for increasing molecular weight and the weight-average molecular weight of the polymer component of the calendered sheets being increased by 5% or more from that of the polyester before calendering.

[0007]

(2) A sheet to be prepared by carrying out calendering of the resin composition described in the above (1).

[0008]

[Preferred Embodiment of the Invention]

The polyester composition of this invention for calendering is characterized by being a composition comprising 100 parts by weight of amorphous polyester, 0.01-5 parts by weight of lubricant and 0.01-50 parts by weight of an agent for increasing molecular weight, and at the same time, the weight-average molecular weight of the composition being increased by 5% or more from that of the polyester. The word "amorphous" in this case is defined as follows. Specifically, in a differential scanning calorimeter (DSC), the temperature is raised from -100°C to 300°C at the rate of $20^{\circ}\text{C}/\text{min}$, subsequently, it is cooled from 300°C to -100°C at the rate of $50^{\circ}\text{C}/\text{min}$, and then, the temperature is raised again from -100°C to 300°C at the rate of

20°C/min. It shows no clear fusion peak in either of those two temperature elevation steps.

[0009]

The amorphous polyester resin of this invention has desirably an aromatic dicarboxylic acid with 8-14 carbon atoms and aliphatic or alicyclic glycol having 2-10 carbon atoms as main components. The main components in this case are components of 50 mole% or higher, preferably 60 mole% or higher and optimally 65 mole% or higher when the total acid components and glycol components are respectively 100 mole%. If it is below 50 mole%, the elongation and mechanical physical properties of sheets prepared by calendering are reduced.

[0010]

The aromatic dicarboxylic acid with 8-14 carbon atoms in the amorphous polyester resin of this invention is preferably terephthalic acid or isophthalic acid. If these dicarboxylic acids are used, the elongation and mechanical physical properties of sheets prepared by calendering are improved further.

[0011]

The amorphous polyester resin of this invention may be copolymerized with known polyhydric carboxylic acids other than terephthalic acid and isophthalic acid such as orthophthalic acid, naphthalenedicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, decanoic acid, dimer acid, cyclohexanedicarboxylic acid, trimellitic acid, etc.

[0012]

The aliphatic or alicyclic glycol with 2-10 carbon atoms in the amorphous polyester of this invention is preferably ethylene glycol, diethylene glycol, neo-pentyl glycol or cyclohexanedimethanol. The combination is ethylene glycol and neo-pentyl glycol among them is preferable because the compatibility with lubricants is good, and both sheet peelability and transparency are liable to become concomitantly satisfactory.

[0013]

The amorphous polyester resin of this invention may be copolymerized with known polyhydric glycols other than ethylene glycol, diethylene glycol, neo-pentyl glycol or cyclohexanedi-methanol such as 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, hexanediol, nonanediol, dimerdiol, bisphenol A ethylene oxide or propylene oxide adduct, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 2-butyl-2-ethyl =-1,3-propanediol, tricyclodecanedimethanol, neopentyl hydroxypivalate, 2,2,4-trimethyl-1,5-pentanediol, trimethylolpropane, etc.

[0014]

The weight average molecular weight of the amorphous polyester resin of this invention is in the range of 30,000-80,000, preferably 35,000-75,000 and optimally 40,000-70,000. If the weight average molecular weight is less than 30,000, the cohesion force of the resin is insufficient, thus, the tensile elongation is insufficient, and it is liable to become fragile. On the other hand, if it is over 80,000, the melt viscosity is increased, the optimal temperature for calendering is also increased, and consequently, the sheet peelability from rollers is reduced.

[0015]

The acid number of the amorphous polyester resin of this invention is below $60 \text{ eq}/10^6 \text{ g}$, preferably below $50 \text{ eq}/10^6 \text{ g}$ and optimally below $40 \text{ eq}/10^6 \text{ g}$. If the acid number is over $60 \text{ eq}/10^6 \text{ g}$, the hydrolysis reaction when the resin is heated for calendering is promoted reducing the mechanical strength of the sheet prepared. Moreover, the sheet peelability from rollers is also reduced as the result of resin hydrolysis.

[0016]

The melt viscosity of the polyester resin composition of this invention at 220°C and shear rate of 100 sec^{-1} is in the range of 6,000-60,000 dPa·sec, preferably in the range of 7,000-50,000 dPa·sec and optimally in the range of 8,000-40,000 dPa·sec. If the melt viscosity is below in the 6,000 dPa·sec, the tackiness of the resin is increased reducing the sheet peelability from rollers.

On the other had, if it is over 60,000 dPa·sec, the melt viscosity is so high that the productivity is reduced, and consequently, it is not practical.

[0017]

Specific examples of the amorphous polyester for calendering of this invention include Toyobo S1173, Eastman Chemical PETG 6763, etc., but it is not necessarily restricted to them.

[0018]

In the production of sheets by carrying out calendering of the polyester resin of this invention, the polyester resin is required to be compounded with a lubricant to improve sheet peelability from rollers. The amount of such a lubricant to be compounded in this invention is in the range of 0.01-5 parts by weight (*sic*). The lower limit is desirably 0.05 part by weight, preferably 0.1 part by weight and optimally 0.2 part by weight. The upper limit is desirably 4.5 parts by weight, preferably 4 parts by weight and optimally 3.5 parts by weight. If the amount of this lubricant is below 0.01 part by weight, it is difficult to achieve the effect improving sheet peelability from rollers. On the other hand, if it is over 5 parts by weight, there are tendencies of the transparency, coloration and printability of sheets prepared being reduced.

[0019]

As a lubricant usable in this invention, there are polyolefin waxes, metal organophosphates, organophosphate esters, esters of adipic acid or azelaic acid and higher aliphatic alcohols, fatty acid amides such as ethylene bisstearateamide, methylene bisstearateamide, etc., glycerol esters of higher fatty acids, pentaerythritol esters of higher fatty acids, higher aliphatic alcohols, higher fatty acids, paraffin or wax derived from petroleum or coal, natural or synthetic polymer ester waxes, higher fatty acid metal soap, etc. They are used alone or as a mixture of 2 or more kinds. The use of metal organophosphates, fatty acid amides and olefin or ester type waxes is preferable because both sheet peelability from rollers and sheet transparency are improved.

[0020]

To improve the takeup ability of a molten sheet from rollers in the case of preparation of sheets from the polyester resin of this invention by carrying out calendering, it is necessary to compound 0.01-50 parts by weight (*sic*) of a molecular weight-increasing agent, which is effective for increasing the weight average molecular weight of the polymer components (those components with a weight average molecular weight of 2,000 or higher) in the sheets after calendering by 5% or more from the weight average molecular weight of the polyester itself. The lower limit is preferably 0.2 part by weight and optimally 0.3 part by weight. The upper limit is preferably 45 parts by weight and optimally 40 parts by weight. If the amount compounded is below 0.01 part by weight, no effect on the takeup ability is observed. On the other hand, if it is over 50 parts by weight, the weight average molecular weight is too high to carry out any measurement (gelation due to so-called three-dimensional cross linking) or reaction with polyester due to excessive reaction points consequently causing the molecular weight-increasing agent to remain unconsumed increasing its plasticizing effect and as a result causing the takeup ability to become insufficient. To allow the sheet takeup improving effect to be exhibited sufficiently, it is necessary to increase the weight average molecular weight after adding the molecular weight-increasing agent by 5% or more, preferably 10% or more and optimally 15% or more from the weight average molecular weight of the polyester. If the weight average molecular weight increase is less than 5% or if it becomes below the original molecular weight, there is no effect observed on the takeup ability.

[0021]

The molecular weight-increasing agent of this invention increasing the weight average molecular weight of the polyester resin of this invention by 5% or more is not especially restricted, but it is preferable to use one selected from those compounds having isocyanate group, epoxy group, carbodiimide group, amino group, carboxyl group, ester group, hydroxyl group, etc., as a substituent reactive to the polyester. Furthermore, those compounds having the same effects on lubricants, antioxidants, UV absorbents, etc., are also included in the scope of this invention. In addition, it is also possible to use those compounds capable of carrying out ring-opening addition polymerization with the polyester terminal such as lactone, lactide, lactam, etc. Those oligomers and polymers having intramolecular reactive substituents are also included. All

intramolecular reactive substituents are not necessarily required to be used for the reaction, and if the weight average molecular weight is increased as a result of the reaction being carried out partially, it is effective on the takeup ability. Incidentally in this case, it is possible to use those forming ionic bonding, coordination bonding, hydrogen bonding, etc., as well as covalent bonding as a result of the reaction. The use of hexamethylene diisocyanate or its trimer tris(hexamethylene diisocyanate) among them is preferable from the viewpoint of versatility and reaction stability.

[0022]

This invention is explained specifically in detail by using application examples as follows, but this invention is not necessarily limited to these application examples. Those results of measurements shown in the application examples were obtained by using the methods as follows.

[0024]

Glass transition temperature: 10 mg of a sample in an aluminum pan was sealed by covering the pan, the temperature was raised at the rate of 20°C/min in a differential scanning calorimeter to measure.

Weight average molecular weight: hexafluoroisopropanol was used as a solvent to carry out gel-permeation chromatography, and the result was obtained as a polystyrene-converted value. The following two products were used as an amorphous polyester for calendering.

Polyester A: saturated copolymeric polyester resin S1173C manufactured by Toyobo Co., Ltd. (glass transition temperature of 76°C and weight average molecular weight of 51,000)

Polyester B: saturated copolymeric polyester resin PETG 6763 manufactured by Eastman Chemical Co. (glass transition temperature of 78°C and weight average molecular weight of 58,000)

[0025]

Application Example 1

In a beaker, 100 parts by weight of the amorphous polyester A, 0.5 part by weight of hexamethylene diisocyanate as a molecular weight-increasing agent and 0.5 part by weight of tridecyl poly(oxyethylene) phosphate zinc salt and 0.1 part styrene-modified polyethylene wax as a mixed lubricant were mixed, and the mixture was kneaded on two chilled rollers of 6 inches diameter heated at 190°C. the mixing was carried out for 5 min by peeling off the resin from the resin from the rollers by using spatula occasionally. Subsequently, the spacing of the rollers was set at 0.3 mm (sheet thickness of 0.3 mm), the molten sheet was pulled away from the rollers in a distance of 30 cm, and the takeup ability was evaluated by observing any slackening of the molten sheet. The peelability of the sheet from the rollers was also observed. the evaluation standards used are as follows. The results obtained are shown in Table 1.

[0026]

Sheet peelability

O: good peelability form rollers, X: strong adhesion to rollers, difficult to peel off and no normal sheet preparation

Sheet takeup ability

⊕: no slack formation at all, O: slight slack formation but no practical problem, X: slack formation due to the own weight of molten sheet and no normal sheet preparation

Transparency

O: extremely transparent, X: inferior transparency

Incidentally, the sign “-” used in the columns for the results of sheet takeup and transparency evaluation indicates no evaluation being carried out due to poor sheet peelability or takeup ability and no normal sheet preparation.

[0027]

Incidentally, the following compounds were used for the molecular weight-increasing agents and lubricants shown in Table 1.

a: hexamethylene diisocyanate

b: tris(hexamethylene diisocyanate) (Colonate HX manufactured by Nippon Polyurethane Industry)

c: tridecyl poly(oxyethylene) phosphate zinc salt

d: styrene-modified polyethylene wax

The unit of those numerals used for the amounts of polyester, molecular weight-increasing agent, lubricant shown in Table 1 is part(s) by weight

[0028]

Application Example 2-4 and Comparative Example 1-3

The composition of amorphous polyester, molecular weight-increasing agent and lubricant of the application example 1 was changed as shown in Table 1. The results obtained are also shown in Table 1.

[0029]

[Table 1]

			Application Example			
			1	2	3	4
Composition	Amorphous polyester	A	100	100		
		B			100	100
	Molecular weight-increasing agent	a	0.5	0.5	0.5	0.3
		b		0.2		0.2
	Lubricant	c	0.5	0.5	1.0	0.5
		d	0.1	0.1	0.2	0.1
Weight average MWt		MWt of amorphous polyester	51,000	51,000	58,000	58,000
		Sheet polymer component MWt	57,000	65,000	65,000	68,000
		Rate of MWt increase (%)*)	12	27	12	17
Evaluation		Sheet peelability	O	O	O	O
		Sheet takeup ability	O	⊕	O	⊕
		Transparency	O	O	O	O

*) Calculated from (molecular weight of polymer components in a sheet – amorphous polyester molecular weight)/amorphous polyester molecular weight; MWt: molecular weight

			Comparative Example		
			1	2	3
Composition	Amorphous polyester	A	100		100
		B		100	
	Molecular weight-increasing agent	a			0.5
		b			
	Lubricant	c	0.5	0.5	
		d	0.1	0.1	
Weight average MWt		MWt of amorphous polyester	51,000	58,000	51,000
		Sheet polymer component MWt	48,000	55,000	59,000
		Rate of MWt increase (%)*)	-6	-5	16
Evaluation		Sheet peelability	O	O	X
		Sheet takeup ability	X	X	-
		Transparency	-	-	-

*) Calculated from (molecular weight of polymer components in a sheet - amorphous polyester molecular weight)/amorphous polyester molecular weight; MWt: molecular weight

[0030]

As apparent from the results shown in Table 1, the results of the evaluation in respective application examples were found to be excellent with respect to sheet peelability, sheet takeup ability and transparency compared with the results obtained in the comparative examples 1 and 2 with no molecular weight-increasing agent added and comparative example 3 with no lubricant added.

[0031]

[Effects of the Invention]

As explained above in detail, the polyester composition of this invention is characterized by being a composition comprising 100 parts by weight of amorphous polyester, 0.01-5 parts by weight of lubricant and 0.01-50 parts by weight of molecular-weight-adjusting agent and at the same time, weight-average molecular weight of the polymer component of the calendered sheets being increased by 5% or more from that of the polyester before calendering. The use of this composition enables excellent calendering of sheets having extremely good characteristics of takeup ability of molten sheets from rollers as well as peelability from rollers, which have been difficult in the previous art and moreover excellent transparency of the sheets prepared.